Recovering the equivalence of ensembles

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Abstract

The equivalence of thermodynamic results in the canonical and the microcanonical ensembles has been questioned in some calculations for spin models with long-range interactions. We show that these claims of inequivalence are related to an inadequate definition of the independent (density) variables in the microcanonical ensemble. We illustrate this point with the example of a simple spin-1 ideal paramagnet, and then revisit the original calculations of Barré, Mukamel, and Ruffo, for a mean-field spin-1 Blume-Capel model. If the microcanonical ensemble is defined in terms of adequate density variables, we show that there is no disagreement with the calculations in the usual canonical ensemble (with fixed thermodynamic field variables).

The equivalence of ensembles, which is one of the hallmarks of modern statistical physics [1][2], has been challenged by Barré, Mukamel and Ruffo [3], in the calculations for a simple mean-field, fully connected, spin-1 Hamiltonian. This work motivated a number of remarks on similar thermodynamic discrepancies between results in the usual canonical and microcanonical ensembles associated with spin model systems with long-range interactions [4].

We show that this claimed inequivalence of ensembles is due to an inadequate definition of the independent variables in the microcanonical ensemble. A proper definition of the microcanonical ensemble is illustrated by analytic calculations for a spin-1 ideal paramagnet. We then revisit the original work of Barré and collaborators for a mean-field version of the spin-1 Blume-Capel

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model, which is known to display a temperature-anisotropy phase diagram with second and first-order transition lines and a tricritical point. If the microcanonical ensemble is defined in terms of the adequate density variables, we show that there is no disagreement with the well-known solutions in the usual canonical ensemble (with fixed temperature and thermodynamic field variables). According to Griffiths and Wheeler [5], we distinguish between "density" variables, given by the ratio of thermodynamic extensive quantities, and "field" variables, which "take on identical values in two phases that are in thermodynamic equilibrium with each other".

1   Ideal paramagnet of spin-1

In this Section, we use a spin-1 ideal paramagnet to give a very simple example of the choice of variables in the usual canonical and the microcanonical formalisms. Consider a spin Hamiltonian given by

$$\mathcal{H} = -H \sum_{j=1}^{N} S_j + D \sum_{j=1}^{N} S_j^2, \tag{1}$$

where H and D are "field variables", and $S_j = -1, 0, +1$, for $j = 1, 2, ..., N$.

1.1   Calculations in the canonical ensemble

In the canonical ensemble (with fixed values of the field variables, H, D, and temperature T), we have the partition function

$$Z = Z(T, H, D) = \sum_{\{S_j\}} \exp\left[\beta H \sum_{j=1}^{N} S_j - \beta D \sum_{j=1}^{N} S_j^2\right] =$$

$$= \left[1 + 2 \exp(-\beta D) \cosh(\beta H)\right]^N, \tag{2}$$

where $\beta = 1/k_B T$. The associated thermodynamic potential per site is given by

$$g = g(T, H, D) = -\frac{1}{\beta} \ln\left[1 + 2 \exp(-\beta D) \cosh(\beta H)\right]. \tag{3}$$

This is a fundamental equation [6] in the $T - H - D$ representation. From this thermodynamic potential, we obtain the equations of state,

$$m = m(T, H, D) = -\left(\frac{\partial g}{\partial H}\right)_{T,D} = \frac{\sinh(\beta H)}{\frac{1}{2} \exp(\beta D) + \cosh(\beta H)}, \tag{4}$$

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where the thermodynamic density m is the dimensionless magnetization per site, $m = \left\langle \sum_{j=1}^{N} S_j \right\rangle / N$, and

$$q = q\left(T, H, D\right) = \left(\frac{\partial g}{\partial D}\right)_{T,H} = \frac{\cosh\left(\beta H\right)}{\frac{1}{2}\exp\left(\beta D\right) + \cosh\left(\beta H\right)}, \tag{5}$$

where the density q is a dimensionless "quadrupole", $q = \left\langle \sum_{j=1}^{N} S_j^2 \right\rangle / N$. The entropy per site is given by the remaining equation of state,

$$s = s\left(T, H, D\right) = -\left(\frac{\partial g}{\partial T}\right)_{H,D} = k_B \ln\left[1 + 2\exp\left(-\beta D\right)\cosh\left(\beta H\right)\right] +$$

$$+ k_B \frac{\beta D \cosh\left(\beta H\right)}{\frac{1}{2}\exp\left(\beta D\right) + \cosh\left(\beta H\right)} - \frac{\beta H \sinh\left(\beta H\right)}{\frac{1}{2}\exp\left(\beta D\right) + \cosh\left(\beta H\right)}. \tag{6}$$

In this usual canonical representation, the thermodynamic densities m, q, and s, are obtained as functions of the fields T, H, and D. The meaning of D as a thermodynamic field can be fully appreciated if we use the spin-1 model to mimic a binary lattice gas of particles, in which case D is related to a chemical potential.

It is now interesting to analyze some features of this ideal spin-1 paramagnet. Using equations (4) and (5), the entropy can be written as

$$s = -\frac{1}{T}g + \frac{D}{T}q - \frac{H}{T}m, \tag{7}$$

which shows that, in this schematic model, the field terms in the effective Hamiltonian do not contribute to the "magnetic internal energy". In other words, the average value of the spin Hamiltonian is a kind of "magnetic enthalpy", which cannot be taken as the internal energy [6]. Equation (7) is just the analogous of the Euler relation for a simple fluid system. It is then straightforward to use this Euler relation, and the expression for the free energy, $g = g\left(T, H, D\right)$, to write the differential form

$$ds = \frac{D}{T}dq - \frac{H}{T}dm, \tag{8}$$

which shows that the entropy per particle s can also be written as a function of the densities m and q. In this special case, we can perform the appropriate calculations to write the analytic expression

$$s = s\left(q, m\right) = -k_B\left(1 - q\right)\ln\left(1 - q\right) - k_B\frac{1}{2}\left(q - m\right)\ln\left(q - m\right) -$$

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$$- k_B \frac{1}{2} \left(q + m \right) \ln \left(q + m \right) + k_B q \ln 2, \tag{9}$$

which is equivalent to a fundamental equation in the microcanonical ensemble (in terms of the densities m and q, and the number of sites N; note the fixed value, $u = 0$, of the internal magnetic energy in this simple paramagnetic model). Incidentally, this expression has the same form as the "entropy to be maximized", given by equation (5) in the article of Barré and collaborators [3].

1.2 Calculations in the microcanonical ensemble

We now show that the same expression for the entropy per particle, $s = s(q, m)$, given by equation (9), can also be obtained in the context of a properly defined microcanonical ensemble, in terms of the densities m and q.

In this simple problem, the number of microscopic configurations is given by

$$\Omega = \Omega \left(N_+, N_0, N_- \right) = \frac{N!}{N_+! N_0! N_-!}, \tag{10}$$

where N is the total number of spins, and N_+, N_0, and N_-, are the numbers of spins up, zero, and down, respectively. Taking into account that

$$N = N_+ + N_0 + N_-, \tag{11}$$

and that,

$$m = \frac{1}{N} \left(N_+ - N_- \right), \qquad q = \frac{1}{N} \left(N_+ + N_- \right), \tag{12}$$

we can write Ω as a function of N, m, and q. In the thermodynamic limit, we show that

$$s = s \left(q, m \right) = \lim_{N \to \infty} \frac{1}{N} k_B \ln \Omega, \tag{13}$$

where $s = s(q, m)$ is a fundamental equation in the entropy representation, given by the same expression, equation (9), which we have already obtained in the context of the canonical ensemble. From this form of the entropy, we obtain the equations of state in the entropy representation,

$$\frac{D}{T} = \left(\frac{\partial s}{\partial q} \right)_m, \qquad \frac{H}{T} = - \left(\frac{\partial s}{\partial m} \right)_q, \tag{14}$$

from which we regain the usual expressions of m and q in the canonical ensemble, given by equations (4) and (5).

At this point we have shown the full equivalence between the canonical and the microcanonical formulations of this simple problem. We can also resort to an alternative (and more general) formulation in the microcanonical ensemble, which turns out to be useful for dealing with short-range interacting systems as well.

In the alternative formulation, we rewrite the canonical partition function in the form

$$Z = Z\left(T, H, D\right) = \sum_{\{S_j\}} \int dm \int dq \, \delta\left(m - \frac{1}{N}\sum_{j=1}^{N} S_j\right) \delta\left(q - \frac{1}{N}\sum_{j=1}^{N} S_j^2\right) \times$$

$$\times \exp\left(\beta H N m - \beta D N q\right), \tag{15}$$

which can also be written as

$$Z = \int dm \int dq \, \Omega\left(q, m, N\right) \exp\left(\beta H N m - \beta D N q\right), \tag{16}$$

where $\Omega\left(q, m, N\right)$ is the number of microstates with fixed values of q, m, and N. We now introduce convenient integral representations of the delta functions. In the thermodynamic limit, we have

$$\Omega \sim \exp\left[N f\left(q, m; k_1, k_2\right)\right], \tag{17}$$

with

$$f = k_1 m + k_2 q + \ln\left[1 + 2\exp\left(-k_2\right)\cosh\left(k_1\right)\right], \tag{18}$$

where the parameters k_1 and k_2 come from the saddle-point equations,

$$\frac{\partial f}{\partial k_1} = \frac{\partial f}{\partial k_2} = 0. \tag{19}$$

The microcanonical entropy is given by $s = s\left(q, m\right) = k_B f$, with k_1 and k_2 obtained from the extremization of the function $f\left(q, m; k_1, k_2\right)$. It is not difficult to show that $k_1 = -\beta H$, and $k_2 = \beta D$, so that equation (18) leads to the same expression of equation (6). Again, we recover the known results in the canonical ensemble.

2   The spin-1 Blume-Capel model

We now consider the special spin system analyzed by Barré and collaborators
[3], given by the fully connected spin-1 Hamiltonian

$$\mathcal{H} = -\frac{J}{2N} \left(\sum_{j=1}^{N} S_j \right)^2 + D \sum_{j=1}^{N} S_j^2, \tag{20}$$

where J and D are positive parameters, and $S_j = +1, 0, -1$ for all sites. In
the canonical ensemble (fixed values of the field variables T and D), we have

$$Z = Z(T, D, N) = \sum_{\{S_j\}} \exp \left[\frac{\beta J}{2N} \left(\sum_{j=1}^{N} S_j \right)^2 - \beta D \sum_{j=1}^{N} S_j^2 \right]. \tag{21}$$

Using a Gaussian identity, we write

$$Z = \left(\frac{\beta J N}{2\pi} \right)^{1/2} \int_{-\infty}^{+\infty} dy \, \exp \left[-\beta N \, g(T, D; y) \right], \tag{22}$$

where

$$g(T, D; y) = \frac{J}{2} y^2 - \frac{1}{\beta} \ln \left[1 + 2 \exp(-\beta D) \cosh(\beta J y) \right]. \tag{23}$$

In the thermodynamic limit, the free energy $g = g(T, D)$ comes from the
minimization of $g(T, D; y)$ with respect to y. We then have

$$g(T, D) = g(T, D; \widetilde{y}), \tag{24}$$

with

$$\widetilde{y} = \frac{\sinh(\beta J \widetilde{y})}{\frac{1}{2} \exp(\beta D) + \cosh(\beta J \widetilde{y})}, \tag{25}$$

and the proviso about the existence of multiple solutions for $\widetilde{y}$ as a function
of the thermodynamic fields T and D.

   We now expand $g(T, D; y)$, given by equation (23), as a power series of
y, with field-dependent coefficients. From this Landau-like expansion, we
obtain the well-known results for the critical line in the $D - T$ space,

$$D = k_B T \ln \left[\frac{2J}{k_B T} - 2 \right], \tag{26}$$

with $1/3 < k_B T/J < 1$, and a tricritical point at $k_B T/J = 1/3$ (and $D/J = (\ln 4)/3$). For $k_B T/J < 1/3$, there is a line of first-order transitions, with the coexistence of a paramagnetic and an ordered phase at well-defined values of the thermodynamic fields T and D. As it is usual in the mean-field models, the location of this first-order border comes from a proper application of a Maxwell construction.

Some simple manipulations lead to the usual equations of state, for the entropy and the quadrupole moment, in the $T - D$ representation,

$$q = \left(\frac{\partial g}{\partial D}\right)_T = \frac{\cosh(\beta J \widetilde{y})}{\frac{1}{2}\exp(\beta D) + \cosh(\beta J \widetilde{y})}, \qquad (27)$$

and

$$s = -\left(\frac{\partial g}{\partial T}\right)_D = k_B \ln\left[1 + 2\exp(-\beta D)\cosh(\beta J \widetilde{y})\right] + \frac{D}{T}q - \frac{J}{T}\widetilde{y}^2, \quad (28)$$

where $\widetilde{y}$ comes form the solutions of equation (25). It easy to see that $\widetilde{y}$ corresponds to the magnetization m per site, $\langle \sum S_j \rangle / N$, but we have to be careful in the region of multiple solutions (and first-order transitions).

2.1 Calculations for the Blume-Capel model in the microcanonical ensemble

As in the work of Barré, Mukamel, and Ruffo [3], we initially write the number of microstates,

$$\Omega = \Omega(N_+, N_0, N_-) = \frac{N!}{N_+! N_0! N_-!}, \qquad (29)$$

where $N = N_+ + N_0 + N_-$ is the fixed number of spins. We now fix the quadrupole density,

$$q = \frac{N_+ + N_-}{N}, \qquad (30)$$

and the internal magnetic energy per site,

$$u = -\frac{J}{2N^2}(N_+ - N_-)^2 = -\frac{J}{2}\left(\frac{N_+ - N_-}{N}\right)^2, \qquad (31)$$

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and write Ω as a function of N, u, and q. In the thermodynamic limit, the entropy is given by

$$s = s(u, q) = \lim_{N \to \infty} \frac{1}{N} k_B \ln \Omega. \tag{32}$$

In this particular mean-field model, the internal energy u is associated with the magnetization m,

$$u = -\frac{J}{2} \left(\frac{N_+ - N_-}{N} \right)^2 = -\frac{J}{2} m^2, \tag{33}$$

so that fixed values of u also correspond to fixed values of m^2. Therefore, the entropy $s = s(u, q)$ is given by

$$s = s(u, q) = -k_B(1-q)\ln(1-q) - k_B\frac{1}{2}[q - m]\ln[q - m] - $$

$$- k_B\frac{1}{2}[q + m]\ln[q + m] + k_B q \ln 2, \tag{34}$$

which is identical to equation (9), for the ideal spin-1 paramagnet, but we now have to take into account that m is a function of u, $m = m(u)$, according to the definition of the internal energy of this mean-field model, given by equation (33). Note that $u < 0$. Also, note the symmetry with respect to $\pm m$.

Given the fundamental equation for this system, $s = s(u, q)$, we write the equations of state in the entropy representation,

$$\frac{1}{T} = \left(\frac{\partial s}{\partial u} \right)_q, \qquad \frac{D}{T} = \left(\frac{\partial s}{\partial q} \right)_u. \tag{35}$$

It is straightforward to show that these equations of state lead to the same expressions for the internal energy u (related to the magnetization m) and the quadrupole moment q, as a function of T and D, which we have already obtained in the context of the usual canonical ensemble. Numerical calculations for the first-order transition border just confirm these findings. In the region of multiple solutions of the mean-field equations, Maxwell´s construction should be properly used to choose the minima of the canonical free energy in terms of D and T (which is equivalent to recovering the convexity of the entropy in the microcanonical ensemble). In contrast to the work of Barré, Mukamel, and Ruffo [3],these calculations indicate that there is full equivalence of ensembles.

2.2 Alternative formulation of the microcanonical ensemble

The equivalence of ensembles can also be shown if we resort to an alternative, and more general formulation of the microcanonical ensemble. In this formulation, we introduce two delta functions to fix the energy u and the quadrupole density q, and rewrite the canonical partition function of the Blume-Capel model,

$$Z = \sum_{\{S_j\}} \int du \int dq\, \delta\left(\left[u + \frac{J}{2N}\left(\sum_{j=1}^{N} S_j\right)^2\right]\right) \delta\left(q - \frac{1}{N}\sum_{j=1}^{N} S_j^2\right) \times$$

$$\times \exp\left[\beta Nu - \beta D N q\right] = \int du \int dq\, \Omega\left(u, q, N\right) \exp\left[-\beta Nu - \beta D N q\right], \quad (36)$$

so that $\Omega\left(u, q, N\right)$ is the number of microstates with fixed values of u, q, and N.

Using an integral representation for the delta functions, it easy to write

$$\Omega\left(u, q, N\right) = \int_{-i\infty}^{+i\infty} \frac{dk_1}{2\pi i} \int_{-i\infty}^{+i\infty} \frac{dk_2}{2\pi i} \exp\left[Nuk_1 + Nqk_2\right] \times$$

$$\times \left(\frac{k_1 J N}{2\pi}\right)^{1/2} \int_{-\infty}^{+\infty} dy \exp\left\{-\frac{1}{2}k_1 J N y^2 + N \ln\left[1 + 2\exp\left(-k_2\right)\cosh\left(k_1 J y\right)\right]\right\}.$$

$$(37)$$

In the thermodynamic limit, we have

$$\Omega\left(u, q, N\right) \sim \exp\left[N f\left(u, q; y, k_1, k_2\right)\right], \quad (38)$$

with

$$f\left(u, q; y, k_1, k_2\right) = k_1 u + k_2 q - \frac{1}{2}k_1 J y^2 + \ln\left[1 + 2\exp\left(-k_2\right)\cosh\left(k_1 J y\right)\right], \quad (39)$$

where the parameters k_1, k_2 and y come from the saddle-point equations,

$$\frac{\partial f}{\partial k_1} = \frac{\partial f}{\partial k_2} = \frac{\partial f}{\partial y} = 0. \quad (40)$$

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The microcanonical entropy is given by $s = s(u, q) = k_B f$, from which we write the equations of state in the entropy representation, $1/T = (\partial s/\partial u)_q$ and $D/T = (\partial s/\partial q)_u$. Using these equations, we have

$$u = -\frac{J}{2}\widetilde{y}^2, \qquad \widetilde{y} = \frac{\sinh(\beta J\widetilde{y})}{\frac{1}{2}\exp(\beta D) + \cosh(\beta J\widetilde{y})}, \qquad (41)$$

and

$$q = \frac{\cosh(\beta J\widetilde{y})}{\frac{1}{2}\exp(\beta D) + \cosh(\beta J\widetilde{y})}, \qquad (42)$$

which are the known expressions in the canonical ensemble.

3   Conclusions

In conclusion, we have shown that claims of inequivalence of ensembles in a class of mean-field spin models can be attributed to an inadequate definition of the independent (density) variables in the microcanonical formalism. As an illustration of an adequate formulation, we performed some analytic calculations for a spin-1 ideal paramagnet. We then revisited the calculations of Barré, Mukamel, and Ruffo [3]. If the microcanonical ensemble is defined in terms of the adequate density variables, we have shown that there is no disagreement with the well-known solutions in the usual canonical ensemble (with fixed thermodynamic field variables).

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